

**Remarks**

Claims 12-13, 26, 28, 79, 111-126, 131-133, 146-148, 150-153 and 155-158 are pending. Applicant requests consideration of the pending claims based on the remarks herein.

**Item 2 of the Advisory Action.**

The Examiner refused entry of the amendment to the claims submitted in Applicant's Response filed 17 July 2003 .

The Examiner maintains that the new limitation of "one or more organic acids" — from "one or more *inorganic acids*" — raises new issues that would require further consideration and/or search.

The amendment to Claim 79 was to correct a typographical error in the claim.

79. A method of cleaning a surface of a semiconductor substrate, comprising the steps of: applying an aqueous solution to selectively remove low-k dielectric material from the surface of the substrate, the aqueous solution effective to selectively remove the low-k dielectric layer at a rate greater than about 2000 angstroms per minute; **the aqueous solution comprising a 2:1 (v/v) ratio of hydrogen fluoride and *one or more inorganic organic acids***, and having a pH of about 2 to about 5.

Furthermore, pending Claims 12, 146 and 152 — which were considered by the Examiner — recite the identical limitation of "an aqueous 2:1 (v/v) solution of hydrofluoric acid *and one or more organic acids*." These claims, in parts relevant to this discussion, recites as follows:

12. A method for surface treating wafer surfaces, comprising the steps of: ...treating the wafer surface...by applying **an aqueous 2:1 (v/v) solution of hydrofluoric acid *and one or more organic acids***....

146. A method of treating a wafer surface, comprising the steps of: ...treating the wafer surface... by applying **an aqueous solution comprising hydrofluoric acid *and one or more organic acids in a ratio of about 2:1 (v/v)***...

152. A method for surface treating wafer surfaces, comprising the steps of: ...treating the wafer surface ... by applying **an aqueous 2:1 (v/v) solution of hydrofluoric acid *and one or more organic acids***...

No new matter was added and no new issue was raised with the amendment to Claim 79. Nor does the amendment require further consideration and/or search — the Examiner having already considered the limitation of "one or more organic acids" in pending Claims 12, 146 and 152.

Accordingly, the Examiner is respectfully requested to withdraw his objection and fully consider the previously made amendment to Claim 79.

**Item 2 of the Advisory Action.**

**Rejection of Claims under 35 U.S.C. 103(a) (Bartlett, Yamazaki, Bell)**

The Examiner maintains that the response did not place the application in condition for allowance and continues his rejection of Claims 12-13, 26, 28, 111-113, 116-119, 123, 125-126, 131-132, and 146-148, 150-153, 155, and 157-158 under Section 103(a) as obvious over USP 4,508,591 (Bartlett) in view of USP 6,198,133 (Yamazaki). The Examiner rejected Claims 114-115, 120-122, 124 and 133 under Section 103(a) as obvious over Bartlett in view of Yamazaki, further in view of USP 6,309,926 (Bell). Again, these rejections are respectfully traversed.

Applicant believes that the Final Rejection is in error because:

- 1) Bartlett fails to teach or suggest all of the limitations of the claims;
- 2) Bartlett does not support the Examiner's rejection;
- 3) Bartlett teaches away from the claimed invention;
- 4) There is no motivation to combine Bartlett with either Yamazaki and/or Bell;
- 5) The Examiner is erroneously applying an "obvious to try" standard to 35 U.S.C. §103(a); and
- 6) The Examiner is erroneously ignoring the limitations in the claims.

**(1) Bartlett fails to teach or suggest all of the limitations of the claims.**

The Examiner has failed to make a *prima facie* case of obviousness because the cited references fail to teach or suggest all of the claim limitations. In particular, Claim 12, in parts relevant to this discussion, recites:

A method for surface treating wafer surfaces, comprising the steps of: treating the wafer surface ... by applying an aqueous 2:1 (v/v) solution of hydrofluoric acid and one or more organic acids...such that the dielectric layer is selectively removed at a rate of greater than about 2000 angstroms per minute.

In addition, Claim 131, in parts relevant to this discussion, recites:

A method of treating a surface of a semiconductor substrate, comprising the step of:  
applying an aqueous solution ... comprising about 63-70% hydrofluoric acid and about 30-36% organic acid....<sup>1</sup>

The Examiner states that the existence of HF in Bartlett's etchant solution resulting from the chemical reaction between the  $\text{NH}_4\text{F}$  + citric acid components reads on the limitation of the claim "regardless of how the etch solution is originally prepared."

The Examiner, in essence, contends that Bartlett, explicitly or inherently, discloses an aqueous etch solution that is a 2:1 (v/v) solution of HF:organic acid(s). The Examiner's contention is in error.

Regarding the explicit disclosure, the Examiner admits that Bartlett teaches the use of an  $\text{NH}_4\text{F}$ :citric acid etchant solution. Thus, Bartlett cannot fairly be said to explicitly disclose or suggest all of the limitations of the pending claims.

Regarding the apparent inherency argument, the Examiner contends that the  $\text{NH}_4\text{F}$  + citric acid etchant solution disclosed in Bartlett includes HF and therefore reads on current Claim 12, as stated in the Advisory Action:

"...the HF component exists in the etchant solution having organic acid by the chemical reaction disclosed by Bartlett in column 2. Since the HF component and organic acid exist in the solution (same chemical component with applicant), this should read on the limitation of the claim regardless how it is prepared...Bartlett teaches that the concentration of HF depends on fluoride ion sources ( $\text{F}^-$ ), which come from ammonium fluoride. Therefore, the examiner concludes that Bartlett implicitly teaches the concentration of HF..."

Such a statement, even if true, fails to meet the standards for establishing an inherent element:

The law requires that inherency may not be established by possibilities or probabilities. The evidence must show that the inherency is necessary and inevitable. *Interchemical Corp. v. Watson*, 111 USPQ 78, 79(d) (D.C. 1956), *aff'd*, 116 USPQ 119 (D.C. Cir. 1958).

The Examiner has not presented any proper evidence that the etchant solution of Bartlett necessarily and inevitably have the currently claimed volume amounts of HF and organic acid(s),

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<sup>1</sup> As described in the specification at page 8, lines 18-24, the solution is formulated with "about 63 to about 70 percent by volume of 49% HF and about 30 to about 36 percent by volume of 50% citric acid and/or other organic acid."

only that etchant solution of Bartlett is not necessarily outside the claimed volume amounts. Consequently, the Examiner has failed to demonstrate that the undisclosed element is necessarily and inevitably included in the teachings of Bartlett.

Furthermore, inherency and obviousness are distinct concepts. *W.L. Gore & Assoc. v. Garlock, Inc.*, 220 USPQ 303, 314 (Fed. Cir. 1983). In order to establish a *prima facie* case of obviousness based on inherent properties, the Examiner must show that the undisclosed elements are not only inevitably and necessarily present, but also that the inherency of the undisclosed properties or elements is obvious to one skilled in the art. *Kloster Speedsteel AB v. Crucible Inc.*, 230 USPQ 81, 88 (Fed. Cir. 1986). The Examiner has presented no arguments or evidence toward establishing that the proposed inherent elements are obviously present. Again, the Examiner has failed to demonstrate that one skilled in the art would recognize that the undisclosed element necessarily and inevitably is included in the teachings of Bartlett. As such, the Examiner has failed to make a *prima facie* case of obviousness of the pending claims over Bartlett.

Furthermore, Bartlett teaches that the etch solution is a dilute fluoride solution.<sup>2</sup>

Bartlett also teaches and claims an etchant solution formulated with **1-20% by volume**  $\text{NH}_4\text{F}$ ,<sup>3</sup> exemplified by a 13%  $\text{NH}_4\text{F}$  content in the Example at cols. 3-4.<sup>4</sup> With regard to Claims 28<sup>5</sup> and 131-133, this does not equate to an etch solution containing about **63-70% by volume HF** (49%).

There is no teaching in Bartlett, either explicitly or implicitly, of an etch solution comprising 2:1 (v/v) HF:organic acid(s) — nor of an etch solution comprising about 63-70% HF.

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<sup>2</sup> "Etchant baths dissolve  $\text{SiO}_2$  in dilute acidic fluoride solutions..." (col. 2, lines 53-54).

<sup>3</sup> See, for example, Claim 1: An etchant solution for the dissolution of silicon dioxide, comprising: an aqueous solution of ammonium fluoride from about 1% to about 20% by volume; and citric acid from about 10 to about 200 grams per liter of aqueous solution.

<sup>4</sup> In the Example at cols. 3-4. Bartlett teaches that a preferred embodiment of the etchant is "constructed by mixing 6600 ml of  $\text{H}_2\text{O}$  with 1000 ml 40% aqueous Ammonium Fluoride and 550 gm Citric Acid." This equates to an etchant solution formulated with 13%  $\text{NH}_4\text{F}$  (40%).

<sup>5</sup> Claim 28: The method of Claim 26, wherein the aqueous solution comprises *about 63 to about 70 % by volume of hydrofluoric acid*, and about 30 to about 36 % by volume of organic acid.

(2) **Bartlett does not support the Examiner's rejection.**

As for the Examiner assertion that the existence of HF in Bartlett's etchant solution resulting from the chemical reaction between the  $\text{NH}_4\text{F}$  + citric acid components reads on the limitations of the claims "regardless of how the etch solution is originally prepared" — Bartlett does not support the Examiner's premise.

It is again noted that the claims recite a solution comprising 2:1 (v/v) HF:organic acid(s) (or about 63-70 % HF in the case of Claims 28 and 131-133).

Assuming, *arguendo*, that the Examiner's premise were true — that the amount of HF in solution is the same regardless of how the etch solution is originally prepared — there should then be *no difference* in etch properties between the various etchants:  $\text{NH}_4\text{F}$ /citric acid —  $\text{NH}_4\text{F}$ /acetic acid —  $\text{NH}_4\text{F}$ /HF.

However, Bartlett particularly teaches that there are distinct differences in the etch properties of these etch solutions. In particular, Bartlett discloses (emphasis added):

- 1)  $\text{NH}_4\text{F}$  + HF etch bath resulted in "*severe etch problems regardless of the proportion of the  $\text{NH}_4\text{F}$  to HF* in the etch bath."<sup>6</sup>
- 2)  $\text{NH}_4\text{F}$  + acetic acid etch bath "showed an improvement with respect to gross resist lifting, however *severe undercutting* was still a major problem."<sup>7</sup>
- 3)  $\text{NH}_4\text{F}$  + citric acid "reduces surface diffusion of the etchant into the resist, thereby resulting in symmetrical lateral etching and uniform patterns."<sup>8</sup>

As disclosed by Bartlett, each of these etch solutions presumably contain HF. However, based on the markedly different etch characteristics — and Bartlett's disclosure that the presence of hydrogen ions supplied by the "complexing agent" (namely citric acid, acetic acid, or HF) controls the etch rate by controlling the concentration of  $\text{HF}_2^-$  and  $\text{HF}$ <sup>9</sup> — each of these etch solutions must necessarily have significantly different concentrations of  $\text{HF}_2^-$  and HF.

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<sup>6</sup> Bartlett at col. 3, lines 8-10.

<sup>7</sup> Bartlett at col. 3, lines 10-13.

<sup>8</sup> Bartlett at col. 3, lines 37-39.

<sup>9</sup> Bartlett at col. 2, line 53 to col. 3, line 4: "...Etch rates depend on the concentration  $\text{HF}_2^-$  and HF...a complexing agent is added which acts as a source of hydrogen ions...The hydrogen ions combine with fluoride ions ... to form  $\text{HF}_2^-$  and HF... The presence of hydrogen ions therefore controls the etch rate by controlling the concentration of  $\text{HF}_2^-$  and HF."

Bartlett does not support the Examiner's premise that Applicant's 2:1 (v/v) HF:organic acid(s) etch solution<sup>10</sup> is *equivalent* to Bartlett's etch solution due to the presence of HF and HF<sub>2</sub>- from the reaction of NH<sub>4</sub>F + citric acid components. Although Bartlett's etch solution contains HF<sub>2</sub>- and HF — it is not necessarily or implicitly a 2:1 (v/v) concentration of HF:organic acid — or an about 63-70% concentration of HF.

**(3) Bartlett teaches away from the claimed invention.**

In addition, Bartlett essentially teaches away from the present invention, i.e., applying an aqueous 2:1 (v/v) solution of HF + organic acid(s) to selectively remove a dielectric layer at a rate greater than about 1000 Å/minute. A reference teaches away when "a person of ordinary skill, upon reading the reference ... would be led in a direction divergent from the path that was taken by the applicant." *In re Gurley*, 313 USPQ2d 1130, 1131 (Fed. Cir. 1994).

Bartlett specifically teaches in the context of the existing art of selectively etching silicon dioxide, and addresses the problem of undercutting and lifting of the photoresist layer during the etch process. Bartlett's solution is to use an etch solution of NH<sub>4</sub>F + citric acid to reduce surface diffusion of the etchant into the resist and achieve symmetrical lateral etching and uniform patterns.<sup>11</sup>

Throughout the disclosure, Bartlett emphasizes the problems and failures with prior art etch baths formulated with HF as a component (i.e., NH<sub>4</sub>F + HF) to etch a masked silicon dioxide layer. Bartlett discusses prior art etch solutions containing HF at col. 1, lines 27-32 and 44-53, at col. 2, lines 45-52, and at col. 3, lines 3-13 (emphasis added):

Silicon dioxide, or glass, is very difficult to etch. Ammonium fluoride has been the primary ingredient in all silicon dioxide etchants. In order to increase the pH stability of such etchants, the prior art has taught the addition of two ingredients, either hydrogen fluoride or acetic acid.

.....  
Prior art solutions to such problems have included: (1) attempting to improve resist adhesion to the silicon dioxide; (2) formulating the best developer conditions; (3) determining the optimum hard bake temperature; and (4) varying the concentration of ammonium fluoride and acetic acid or hydrogen fluoride in the etchant solution. Each of these attempted solutions has failed to resolve the problem of maintaining very narrow line widths to the high degree of uniformity and accuracy demanded by the VLSI process.

<sup>10</sup> An about 63-70% HF in the case of claims 28 and 131-133.

<sup>11</sup> Bartlett at col. 3, lines 35-39.

With the mask in place, the chemical processing begins. Silicon dioxide may be removed where it is not protected by the photoresist using one of two methods, either a 'dry' plasma etch or a 'wet' etchant bath. When the prior art 'wet' etchant bath is used, severe undercutting and resist lifting occurred as shown in FIG. 4. More desirable results are obtained, as illustrated in FIG. 5, when the silicon dioxide is etched with a process using the etchant of the present invention.

In the prior art, acetic acid or **hydrogen fluoride** was predominately used as the complexing agent. Since the amount of undercutting and resist lifting which occurs during the etch process also depends upon the chemistry of the photoresist/oxide interface, VLSI processing involving a PCM technique encountered severe etch problems regardless of the proportion of the  $\text{NH}_4\text{F}$  to  $\text{HF}$  in the etch bath. Acetic acid/ $\text{NH}_4\text{F}$  solutions showed an improvement with respect to gross resist lifting, however severe undercutting was still a major problem. ...

Bartlett twice emphasized that severe etch problems remained regardless of the amount of  $\text{HF}$  in an etch bath formulated with  $\text{HF}$  as a component (i.e.,  $\text{NH}_4\text{F} + \text{HF}$ ), and that varying the concentration of  $\text{HF}$  in the etchant solution did not resolve severe etch problems. However, such problems were resolved or reduced using etch solutions of  $\text{NH}_4\text{F} + \text{acetic acid}$  and  $\text{NH}_4\text{F} + \text{citric acid}$ — which eliminated  $\text{HF}$ . As such, Bartlett teaches away from the use of an etch solution formulated with hydrogen fluoride ( $\text{HF}$ ) and an organic acid.

Based on the teaching of Bartlett, one of skill in the art would have no motivation or basis to utilize an etch solution formulated with  $\text{HF} + \text{organic acid(s)}$  to surface treat or clean a wafer surface as claimed.

**(4) There is no motivation to combine Bartlett with either Yamazaki and/or Bell.**

Obviousness cannot be established by combining the teachings of the prior art to produce the claimed invention, absent some teaching or suggestion supporting the combination. Here, the teachings of Yamazaki, Bell and Bartlett are inconsistent and contain no such suggestion or incentive in support of the combination.

Yamazaki is directed to an etch solution of  $\text{HF}:\text{NH}_4\text{F}:\text{acetic acid}$ . By contrast, Bartlett is directed to an etch solution of  $\text{NH}_4\text{F}:\text{citric acid}$ . In fact, Bartlett explicitly and clearly teaches the use of acetic acid is undesirable because of etch problems of severe undercutting,<sup>12</sup> and that the use of  $\text{HF}$  regardless of the concentration did not solve etch problems.<sup>13</sup> Therefore, Bartlett

<sup>12</sup> Bartlett at col. 3, lines 3-13 (emphasis added): "In the prior art, acetic acid or hydrogen fluoride was predominately used as the complexing agent...Acetic acid/ $\text{NH}_4\text{F}$  solutions showed an improvement with respect to gross resist lifting, however severe undercutting was still a major problem. ..."

<sup>13</sup> Bartlett at col. 3, lines 3-13 (emphasis added): "...encountered severe etch problems regardless of the proportion of the  $\text{NH}_4\text{F}$  to  $\text{HF}$  in the etch bath."

warns against Yamazaki's HF:NH<sub>4</sub>F:acetic acid etch solution. In the face of this, one skilled in the art would not be expected to combine the teachings of Yamazaki with Bartlett.

Bell is directed to a dry etch CH<sub>4</sub>F chemistry,<sup>14</sup> whereas both Bartlett and Yamazaki are directed to wet etch chemistries. One skilled in the art would have no incentive to combine the teachings of Bell with Bartlett and Yamazaki.

The Examiner has not combined the cited references based on any teaching or suggestion in any of the references, but rather upon his own analysis.

(5) **The Examiner is erroneously applying an "obvious to try" standard to 35 U.S.C. §103(a).**

The Examiner's statement<sup>15</sup> that it would be obvious "to perform routine experiment to obtain optimal concentration ratio and etch rate" based on the disclosure in Yamazaki and/or Bell is an improper basis for rejection of the claims.

With respect to obvious to try, two types of errors are generally recognized. *In re Fine*, 5 U.S.P.Q.2d 1596, 1599 (Fed. Cir. 1988), *In re O'Farrell*, 7 U.S.P.Q.2d 1673 (Fed. Cir. 1988). The error committed by the Examiner is the case in which what "is obvious to try" is to vary all parameters or try each of numerous choices until successful without indication in prior art as to which parameters were critical or which choices were likely to be successful.

The Examiner cited Yamazaki as teaching "a typical removal rate of silicon oxide (low-k dielectric) at 800-1000 Å"<sup>16</sup> and maintains that it would be obvious to modify Bartlett's solution to achieve an etch rate of greater than 1000 Å/min.

However, Yamazaki gives no guidance to modifying an etch solution made of NH<sub>4</sub>F/citric acid as explicitly taught by Bartlett. Yamazaki specifically teaches an etch solution made of HF:NH<sub>4</sub>F:acetic acid.

The mere disclosure in Yamazaki of an etch solution having a removal rate of 800-1000 Å/minute does not provide an art worker with any guidance for increasing the etch rate

<sup>14</sup> See Bell at col. 10, lines 23-31.

<sup>15</sup> Office Action (mailed May 29, 2003 (paper no. 10) at page 4, lines 11-12; page 5, lines 5-6; page 6, line 18; and page 7, lines 4-5.

<sup>16</sup> Yamazaki at col. 6, lines 38-49 (emphasis added): "A base silicon oxide film 602 having a thickness of 2000 Å is formed on a glass substrate ... A typical etching rate is 800 to 1100 Å/minute using acetic acid-added buffer hydrofluoric acid (ABHF) (hydrofluoric acid: ammonium fluoride: acetic acid=1:50:50) at 23°C.



of an etch solution made of  $\text{NH}_4\text{F}$ /citric acid — which is clearly different from Yamazaki's etch solution of  $\text{HF}:\text{NH}_4\text{F}:\text{acetic acid}$ .

Likewise, Yamazaki's disclosure fails to provide any guidance for achieving Applicant's etch solution of  $\text{HF}$ :organic acid(s) having an etch rate of greater than about 1000 Å/minute.

As for Bell — Bell is directed to a dry etch  $\text{CH}_3\text{F}$  chemistry and gives no guidance for modifying wet chemistry components to vary selectivity.

**(6) The Examiner is erroneously ignoring the limitations in the claims.**

The Examiner asserts that the term "comprising" in the claim allows for the inclusion of unspecified ingredients — concluding that Yamazaki's teaching of three ingredients ( $\text{HF}$ ,  $\text{NH}_4\text{F}$ , acetic acid) reads on the claims.

The Examiner ignores the limitation in the claims of 2:1 (v/v) ratio of  $\text{HF}$ :organic acid.

Yamazaki specifically teaches a 1:50:50 ratio of  $\text{HF}:\text{NH}_4\text{F}:\text{acetic acid}$ . Yamazaki does not teach or suggest the claimed ratio of ingredients to accomplish Applicant's method of surface treating (cleaning) wafer surfaces to selectively remove a dielectric layer at a high rate of removal (e.g., greater than about 1000 Å/min.).

In sum, Bartlett, either alone or combined with Yamazaki and/or Bell, does not teach or suggest the use of an etch solution of  $\text{HF}$ :organic acid(s) to remove dielectric material — particularly a **2:1 (v/v) solution** of  $\text{HF}$ :organic acid(s) which achieves rapid and selective removal of dielectric, particularly at a rate of greater than about 1000 Å/minute.

Accordingly, withdrawal of the rejections of the claims is respectfully requested.

**Rejection of Claims under 35 U.S.C. 103(a) (Anzaki, Kwag)**

The Examiner's rejection of Claim 79 under Section 103(a) as obvious over USP 6,277,507 (Anzaki) in view of USP 6,232,228 (Kwag) is considered moot in view of the amendment to the claim.

As presented hereinabove at page 2, Claim 79 has been amended to recite that the aqueous solution comprises a 2:1 (v/v) ratio of hydrogen fluoride and one or more organic acids, which amendment should be properly entered and considered.

Both Anzaki and Kwag are directed toward etch solutions of HF and an inorganic acid. As admitted by the Examiner, Anzaki describes a wet etch solution consisting of HF, nitric acid, and water. Kwag discloses a solution of HNO<sub>3</sub>, HF, and water.

Neither reference provides any information for an etch solution selective to a dielectric material layer comprising HF and an organic acid.

Accordingly, withdrawal of this rejection is respectfully requested.

**Extension of Term.** The proceedings herein are for a patent application and the provisions of 37 CFR § 1.136 apply. Applicant believes that no extension of term is required. However, this conditional petition is being made to provide for the possibility that Applicant has inadvertently overlooked the need for a petition for extension of time. If any extension and/or fee are required, please charge Account No. 23-2053.

Based on the above remarks, the Examiner is respectfully requested to reconsider and withdraw the rejections of the claims. It is submitted that the present claims are in condition for allowance, and notification to that effect is respectfully requested.

Respectfully submitted,



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